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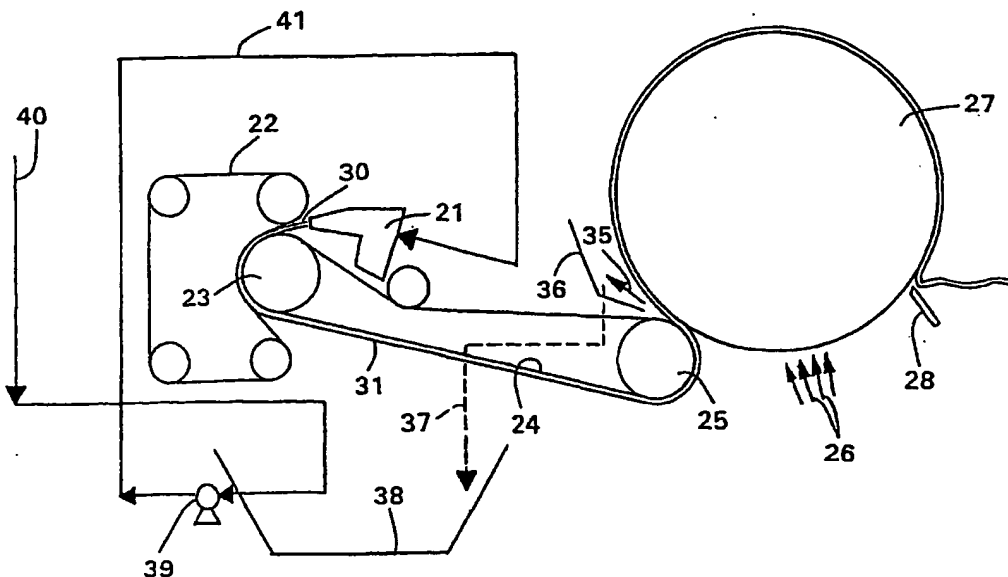
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[Continued on next page]

(54) Title: **HIGH OPACITY TISSUE PRODUCTS**



(57) Abstract: The present invention is generally directed to a tissue product exhibiting an increased opacity and a method for creating the same. The increased opacity is a result of the incorporation of nonparticulate fillers into the tissue product. Specifically, the nonparticulate fillers used in the process of the present invention are hollow microsphere pigments which may be incorporated into the tissue product in either the wet end or the dry end of the manufacturing process for tissue products.



**WO 01/38639 A1**



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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## HIGH OPACITY TISSUE PRODUCTS

**Field of the Invention**

5       The present invention generally relates to the incorporation of nonparticulate fillers into tissue products such as bath tissue, facial tissue, and towels for enhancing opacity without resulting in decreased softness and increased stiffness. More particularly, the present invention is directed to the incorporation of hollow microsphere pigments into tissue products in either the wet end or the  
10       dry end of the manufacturing process for tissue products.

**Background of the Invention**

      Opacity is an important property of tissue products and is directly related to basis weight. As technology develops to allow the formation of acceptable tissue products at lower basis weights,  
15       maintaining the opacity, or "see-through", of tissue products becomes a key issue. Low opacity in a tissue product may cause the consumer to perceive the tissue as weak, flimsy, or of poor quality in general.

      A traditional method of enhancing opacity in paper products is the addition of particulate fillers. Such particulate fillers may include  
20       titanium dioxide, Kaolin, calcium carbonate, and the like, and may be added in the wet end of tissue formation or as a post-treatment to the formed tissue.

      The use of such particulate fillers in tissue products, however, typically increases the abrasiveness and stiffness of the tissue  
25       products while decreasing their softness. Furthermore, particulate fillers are usually inorganic fillers that leave a residue when the product is ashed, thus resulting in a further disadvantage of employing such particulate fillers.

      Nonparticulate fillers are known in the industry for their ability  
30       to improve the opacity of fine papers. Specifically, nonparticulate fillers such as hollow microsphere pigments have been used to improve the opacity of newsprint and other such papers. However, the characteristics of softness and low stiffness are not of great importance in this end of the paper industry.

35       Such hollow microsphere pigments have not been commonly

incorporated into tissue products. On the other hand, U.S. Patent No. 4,619,734 to Andersson does disclose a sanitary paper web having high bulk and high softness that contains expanded microspheres of thermoplastic material. Yet, the incorporation of these expanded microspheres results in a decrease of the tensile strength. Also, the web product described in Andersson is bulky, and the opacity of the product is not improved to desired levels. Thus, a need currently exists for a process involving the incorporation of nonparticulate fillers, specifically hollow microsphere pigments, into tissue products in order to impart superior opacity to the tissue products without sacrificing the softness of the products and without increasing the abrasiveness and stiffness of the products.

#### **Summary and Objects of the Invention**

It is an object of the present invention to provide tissues products with increased opacity.

It is another object of the present invention to create tissue products having opacity levels greater than the opacity levels of tissue products made with particulate fillers.

It is still another object of the present invention to form tissue products having improved tactile properties, such as softness and tensile strength, as compared to tissue products made with particulate fillers.

Some of the above-mentioned objects and, perhaps, other objects are accomplished by incorporating nonparticulate fillers in the wet end of a tissue manufacturing process or as a post-treatment additive to a formed tissue. In certain embodiments, a cationic starch retention aid may be added to the tissue product along with the nonparticulate filler in order to enhance retention of the filler.

In some embodiments, the nonparticulate fillers may be incorporated into tissue products during the dry end of a tissue manufacturing process as a post-treatment additive. For example, the fillers may be printed or sprayed onto the tissue, with or without the inclusion of a binder.

These and other features, aspects and advantages of the present invention will become better understood with reference to the

following description and appended claims. The accompanying drawing, which is incorporated in and constitutes a part of this specification, illustrates an embodiment of the invention and, together with the description, serves to explain the principles of the invention.

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#### **Brief Description of the Drawing**

A full and enabling disclosure of the present invention, including the best mode thereof, to one of ordinary skill in the art, is set forth more particularly in the remainder of the specification, including reference to the accompanying drawing, in which:

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FIG. 1 is a schematic flow diagram of a conventional wet-pressed tissue making process useful in the practice of this invention.

#### **Detailed Description of Preferred Embodiments**

Reference now will be made in detail to the embodiments of the invention, one or more examples of which are set forth below.

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Each example is provided by way of explanation of the invention, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment, can be used on another embodiment to yield a still further embodiment.

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Thus, it is intended that the present invention cover such modifications and variations as come within the scope of the appended claims and their equivalents. Other objects, features and aspects of the present invention are disclosed in or are obvious from the following detailed description. It is to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present invention, which broader aspects are embodied in the exemplary constructions.

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The present invention involves the incorporation of nonparticulate fillers, such as hollow microsphere pigments, into sanitary bath tissue, facial tissue, and other such tissue products for the purpose of increasing opacity without substantially decreasing softness and strength. The fillers may be incorporated into the tissue

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products either during the wet end of the manufacturing process or as a post-formation additive. The resulting tissue products exhibit opacity levels greater than the opacity levels of tissue products made with particulate fillers such as titanium dioxide or Kaolin. The opacity  
5 levels of the products of the present invention are also greater than the opacity levels of prior art tissue products containing nonparticulate fillers such as the products described in the above-described patent to Andersson.

Specifically, in the process of the present invention, hollow  
10 microsphere pigments sold commercially under the trade name ROPAQUE and manufactured by Rohm and Haas may be incorporated into facial and bath tissue. The pigments are added, in one embodiment, at an amount of from about 20 pounds/ton to about 100 pounds/ton. In another embodiment, the nonparticulate filler is  
15 added in an amount of from about 20 pounds/ton to about 60 pounds/ton. More specifically, the hollow microsphere pigments may be added at an amount of from about 0.5% to about 10% based on the dry weight of the tissue product.

An important advantage of the present invention lies in the fact  
20 that the tensile strength of a tissue product is retained when the nonparticulate fillers are added to such tissue products according to the method described herein. In fact, when about 0.5% to about 10% of the hollow microsphere pigments are added to a tissue product, the tensile strength of the resulting tissue product is substantially similar  
25 to the tensile strength of a tissue product without the fillers. Prior art methods of incorporating nonparticulate fillers into tissue products (such as the one described in Andersson) result in products with decreased tensile strength.

Another significant advantage of products of the present  
30 invention involves the decreased bulk of such products. Prior art methods involve the use of thermally expanded microspheres and result in products having high bulk. Conversely, products of the present invention are significantly less bulky in that the hollow microsphere pigments used herein are not thermally expanded.

35 The addition of the nonparticulate fillers in the wet end of a

tissue manufacturing process is effected by adding the hollow microsphere pigments to the tissue product at some point in the process prior to complete web formation. Typically, tissue products are made according to widely known papermaking-type processes. For example, U.S. Patent No. 5,129,988 to Farrington, Jr.; U.S. Patent No. 5,772,845 to Farrington, Jr. et al.; and U.S. Patent No. 5,494,554 to Edwards et al. disclose various tissue-making methods and methods for forming multi-layered paper webs. Such patents are incorporated herein in their entireties by reference thereto.

Figure 1 is a schematic flow diagram of a conventional wet-pressed tissue making process useful in the practice of this invention, although other tissue making processes can also benefit from the method of this invention, such as thorough drying or other non-compressive tissue making processes. The specific formation mode illustrated in Figure 1 is commonly referred to as a crescent former, although many other formers well known in the papermaking art can also be used. Shown is a headbox 21, a forming fabric 22, a forming roll 23, a paper making felt 24, a press roll 25, a spray boom 26, a Yankee dryer 27, and a creping blade 28. Also shown, but not numbered, are various idler or tension rolls used for defining the fabric runs in the schematic diagram, which may differ in practice. As shown, the headbox 21 continuously deposits a stock jet 30 between the forming fabric 22 and felt 24, which is partially wrapped around the forming roll 23. Water is removed from the aqueous stock suspension through the forming fabric by centrifugal force as the newly-formed web traverses the arc of the forming roll. As the forming fabric and felt separate, the set web 31 stays with the felt and is transported to the Yankee dryer 27.

At the Yankee dryer, creping chemicals may be continuously applied in the form of an aqueous solution to the surface of the Yankee dryer on top of the residual adhesive remaining after creping. The creping chemicals can include one or more dry strength agents. The solution is applied by any conventional means, such as a spray boom 26 which evenly sprays the surface of the dryer with the creping adhesive solution. The point of application on the surface of the dryer

is immediately following the creping doctor blade 28, permitting sufficient time for the spreading and drying of the film of fresh adhesive before contacting the web in the press roll nip.

5           The wet web 31 is applied to the surface of the dryer by means of the press roll or pressure roll 25 with an application force typically of about 200 pounds per square inch (psi). The incoming web is nominally at about 10% consistency (range from about 8 to about 20%) at the time it reaches the press roll. Following the pressing and dewatering step, the consistency of the web is at or above about 30%.  
10       The side of the web in contact with the surface of the Yankee dryer is referred to herein as the "dryer side" of the web. The opposite side of the web is referred to as the "air side" of the web. Sufficient Yankee dryer steam power and hood drying capability are applied to the web to reach a final moisture content of about 2.5% or less.

15           Also illustrated in Figure 1 is the white water recycle system. At the press roll nip, white water effluent 35 expressed from the wet web is collected in catch pan 36. Because of the presence of a substantial amount of water in the pressure roll nip, some of the dry strength agent is transferred from the surface of the Yankee into the  
20       white water, which also contains fines. The collected white water 37 drains into wire pit 38. Thick stock 40 having a consistency of about 2 percent is diluted with white water at the fan pump 39 to a consistency of about 0.1 percent. The diluted stock 41 is subsequently injected into the headbox 21 to form the wet web.

25           The hollow microsphere pigments may be added anywhere in the wet end of the tissue making process. For example, the pigments may be added to the headbox 21, prior to headbox 21 in a separate apparatus that then flows the pigments into contact with the pulp furnish (sometimes referred to as stock suspension) in the headbox  
30       21, or after the headbox 21 as a direct additive to the pulp furnish being carried between forming fabric 22 and felt 24.

          Papermaking fibers for making the tissue product webs of this invention include any natural or synthetic fibers suitable for the end use products listed above including, but not limited to: nonwoody  
35       fibers, such as abaca, sabai grass, milkweed floss fibers, pineapple

leaf fibers; softwood fibers, such as northern and southern softwood kraft fibers; hardwood fibers, such as eucalyptus, maple, birch, aspen, or the like. In addition, furnishes including recycled fibers may also be utilized. In making the tissue products, the fibers are formed into a pulp furnish by known pulp stock formation processes.

Softening agents, sometimes referred to as debonders, can be added to the tissue making process to enhance the softness of the tissue product. Such softening agents can be incorporated with the fibers before, during or after dispersing the fibers in the furnish. Such agents can also be sprayed or printed onto the web after formation, while wet, or added to the wet end of the tissue machine prior to formation. Suitable softening agents include, without limitation, fatty acids, waxes, quaternary ammonium salts, dimethyl dihydrogenated tallow ammonium chloride, quaternary ammonium methyl sulfate, carboxylated polyethylene, cocamide diethanol amine, coco betane, sodium lauryl sarcosinate, partly ethoxylated quaternary ammonium salt, distearyl dimethyl ammonium chloride, polysiloxanes and the like. Examples of suitable commercially available chemical softening agents include, without limitation, Berocell 596 and 584 (quaternary ammonium compounds) manufactured by Eka Nobel Inc., Adogen 442 (dimethyl dihydrogenated tallow ammonium chloride) manufactured by Sherex Chemical Company, Quasoft 203 (quaternary ammonium salt) manufactured by Quaker Chemical Company, and Arquad 2HT-75 (di(hydrogenated tallow) dimethyl ammonium chloride) manufactured by Akzo Chemical Company. Suitable amounts of softening agents will vary greatly with the species of pulp selected and the desired characteristics of the resulting tissue product. Such amounts can be, without limitation, from about 0.05 to about 1 weight percent based on the weight of fiber, more specifically from about 0.25 to about 0.75 weight percent, and still more specifically about 0.5 weight percent.

Furthermore, a cationic starch may be added at a level of up to 1% of the nonparticulate filler in order to enhance retention of the fillers within the tissue products. In one embodiment of the present invention, such a cationic retention aid is added after the fan pump at

a level of up to 2 pounds/ton of total furnish in order to adhere the pigment to the pulp. The level of retention aid needed for good retention of the nonparticulate filler may vary considerably depending on the charge of the overall system. In certain embodiments of the present invention, the level of cationic retention aid is about 1  
5 pound/ton or less.

In other embodiments of the present invention, the described nonparticulate fillers may be incorporated into tissue products in the dry end. In such embodiments, the fillers may be provided to tissue  
10 products by conventional post-formation applying means such as printing, brushing, spraying, dipping, doctor blading, foamed emulsion, gravure roll polymer emulsion, padding, nip-pressure binder pick-up, direct or offset gravure printing and the like. The use of a binder in conjunction with the pigments may be necessary in such  
15 post-formation applications, particular the various printing and brushing techniques, but not necessary in techniques such as spraying. It should be understood that the present invention is not limited to any particular application process for applying the pigments to a formed treatment product.

20 These and other modifications and variations to the present invention may be practiced by those of ordinary skill in the art, without departing from the spirit and scope of the present invention, which is more particularly set forth in the appended claims. In addition, it should be understood that aspects of the various embodiments may  
25 be interchanged both in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention so further described in such appended claims. Therefore, the spirit and scope of the appended claims should not be limited to the description  
30 of the preferred versions contained therein.

**WHAT IS CLAIMED IS:**

1. A process for enhancing the opacity of tissue products comprising the step of adding a nonparticulate filler to said tissue products while said tissue products are being formed.
- 5 2. A process according to claim 1 wherein said nonparticulate filler comprises a hollow microsphere pigment.
3. A process according to claim 1 wherein said tissue products are chosen from the group consisting of sanitary bath tissue, facial tissue, and low basis weight towels.
- 10 4. A process according to claim 1 wherein said nonparticulate filler is added to said tissue products in an amount of from about 20 pounds/ton to 100 pounds/ton.
5. A process according to claim 1 further including the step of adding a cationic starch retention aid to said tissue products while  
15 said tissue products are being formed so that retention of said nonparticulate filler within said tissue products is increased.
6. A process according to claim 5 wherein said cationic starch retention aid is added to the pulp furnish at an amount of about 2 pounds/ton or less.
- 20 7. A process for enhancing the opacity of tissue products comprising the step of treating a tissue product with a nonparticulate filler after said tissue product has been formed.
8. A process according to claim 7 wherein said nonparticulate filler comprises a hollow microsphere pigment.
- 25 9. A process according to claim 7 wherein said nonparticulate filler is added to said tissue products in an amount of from about 20 pounds/ton to 100 pounds/ton.
10. A process according to claim 7 wherein said nonparticulate filler is added to said tissue products in an amount of  
30 from about 0.5% to about 10% based on the dry weight of said tissue products.
11. A process according to claim 7 wherein said nonparticulate filler is printed onto said tissue products after formation thereof.
- 35 12. A process according to claim 11 wherein a binder is incorporated with said nonparticulate filler during the printing process.

13. A process according to claim 7 wherein said nonparticulate filler is sprayed onto said tissue products after formation thereof.

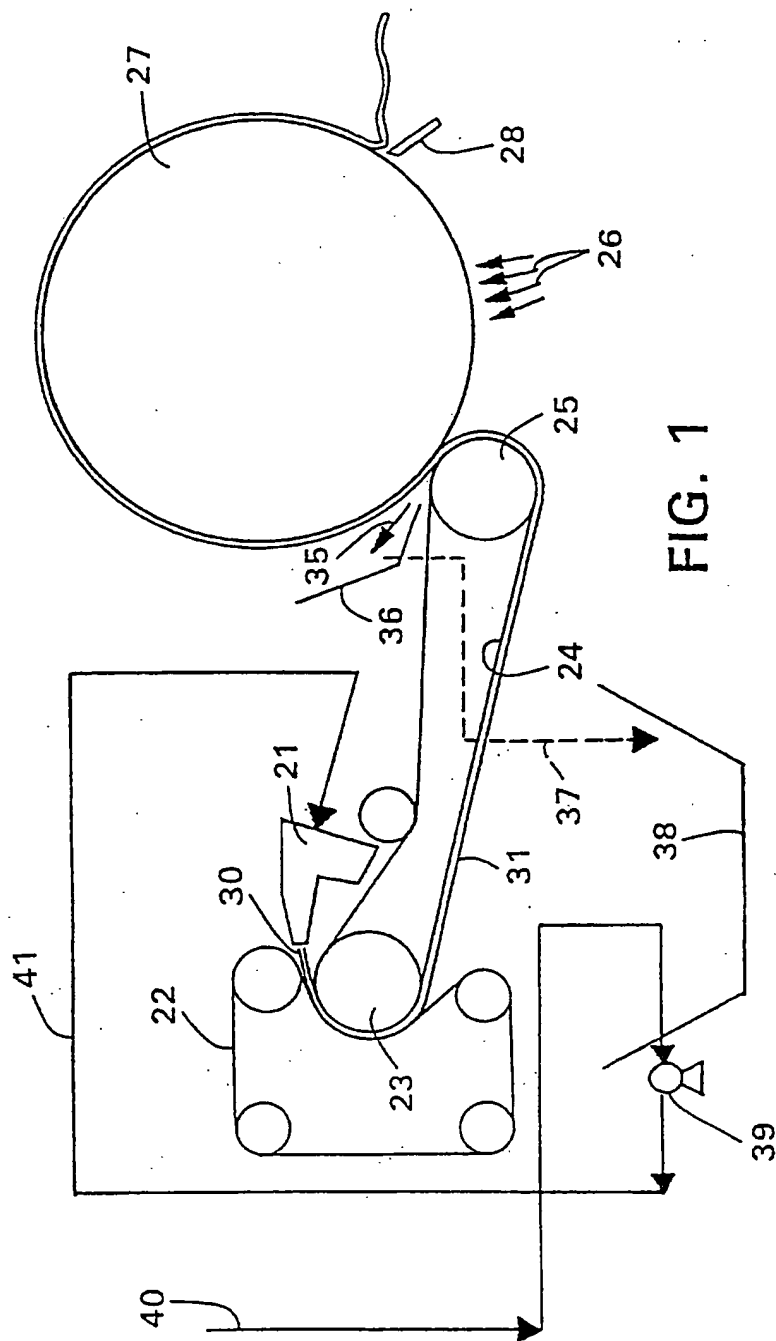
5 14. A tissue product with enhanced opacity having a nonparticulate fillers therein.

15. A tissue product according to claim 14 wherein said nonparticulate filler comprises a hollow microsphere pigment.

10 16. A tissue product according to claim 15 wherein said tissue product exhibits opacity levels greater than the opacity levels of an identical tissue product having a particulate filler therein.

17. A tissue product according to claim 15 wherein said tissue product is softer than an identical tissue product having a particulate filler therein.

15 18. A tissue product according to claim 15 wherein the tensile strength of said tissue product is substantially similar to the tensile strength of an identical tissue product having no filler therein.



# INTERNATIONAL SEARCH REPORT

In ternational Application No

PCT/US 00/32162

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 D21H21/28

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAPERCHEM

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 619 734 A (ANDERSSON INGMAR A) 28 October 1986 (1986-10-28) cited in the application the whole document	1-4, 14, 15
X	US 5 902 669 A (BOATMAN DONN NATHAN ET AL) 11 May 1999 (1999-05-11) column 9, line 61 -column 10, line 15	1-3, 7-9, 14, 15
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A	FR 1 401 629 A (PAPIRINDUSTRIENS FORSKNINGSINSTITUTT) 13 October 1965 (1965-10-13)	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

\*A\* document defining the general state of the art which is not considered to be of particular relevance

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\*O\* document referring to an oral disclosure, use, exhibition or other means

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\*&\* document member of the same patent family

Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/32162

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